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Self-organized supermolecules based on conducting polyaniline and hydrogen bonded amphiphiles

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Abstract

We describe a concept to achieve comb-like supermolecules by hydrogen bonding camphor sulphonic acid (CSA) doped polyaniline (PANI) to *4*-Hexyl resorcinol (Hres). The supermolecules, in turn, self-organize to form cylindrical nanostructures with the distances of 35 Å between the cylinders. The self-organized structures show improved conductivity in the bulk.

Keywords: polyaniline and derivatives, self-organization in macromolecules, supermolecules, recognition

1. Introduction

Self-organization based on competing interactions allows nanoscale polymeric structures[1] with interesting functional or controllable properties[2,3]. A simple prototype is provided by diblock copolymers which form self-organized spherical, cylindrical, gyroid, and lamellar structures[4]. Hairy rods are comb copolymers which have rigid backbones and a dense set of repulsive side chains (such as alkyl tails) as covalently bonded to the backbone[5]. They form typically lamellar or cylindrical structures with a periodicity of 20-30 Å[5,6].

Supermolecules are moieties held together by molecularly matching physical bonds (recognition)[7]. To achieve comb-shape supermolecules, ionic interactions[8, 9], coordination[10], and hydrogen bonds[11,12] can be used to bond the repulsive side chains to the backbone in order to allow polymer-amphiphile supermolecules. Polyaniline, protonated with a strong acid[13] is known to form a conducting polymeric salt. Self-organized lamellar structure of conjugated polyaniline has been observed, using alkyl containing strong acid[14].

Our aim was to form supermolecules of conducting PANI-salts and amphiphiles with matching physical bonds to allow conducting self-organized cylinders to achieve "molecular wires".

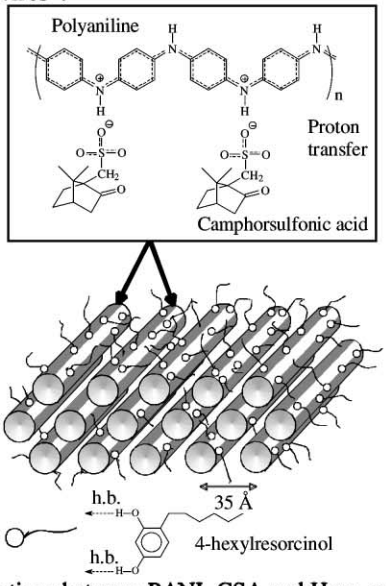

Fig 1. Interactions between PANI, CSA and Hres, and formation of self-organized hexagonal cylindrical structure. The hydrogen bonds (h.b.) probably take place to the sulphonates and the amines (so far not known in detail).

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2. Results and Discussion

Highly conducting films of $PANI(CSA)_{0.5}$ complexes can be cast from *m*-cresol solution[15]. Generally, a longer repulsive alkyl chain (than the methyl contained in *m*-cresol) would be needed to achieve self-organization[11]. However, increasing the alkyl chain length in phenols typically leads to macroscopic phase separation in the case of $PANI(CSA)_{0.5}$. In this work, another hydroxyl group is introduced to overcome this problem to promote hydrogen bonding capability and *4*-Hexyl resorcinol (Hres) proves to have a feasible combination between the repulsion (alkyl tail) and the attraction (hydrogen bondings). In SAXS measurements, sharp peaks ($1q_1$, $\sqrt{3}q_1$ and $2q_1$) indicate that $PANI(CSA)_{0.5}(Hres)_y$ supermolecules form a self-organized hexagonal cylindrical structure with the distances between the cylinders of ca. 35 Å (Fig. 2). Increasing the mole fraction of Hres, the distances increase from 34.7 Å to 36.8 Å.

$PANI(CSA)_{0.5}$ cast from formic acid shows relatively poor conductivity (see Fig. 3) as formic acid is a worse solvent as *m*-cresol. Note that all samples have been cast from highly volatile formic acid instead of *m*-cresol as the latter solvent would have been difficult to remove completely from the samples containing also another phenol Hres. However, the conductivities of $PANI(CSA)_{0.5}(Hres)_y$ supermolecules increase about two decades to 1 S/cm when a mole fraction of Hres is increased and the cylindrical structure is formed. A probable explanation is that the conformations of $PANI(CSA)_{0.5}$ chains are more extended upon confinement in the cylinders.

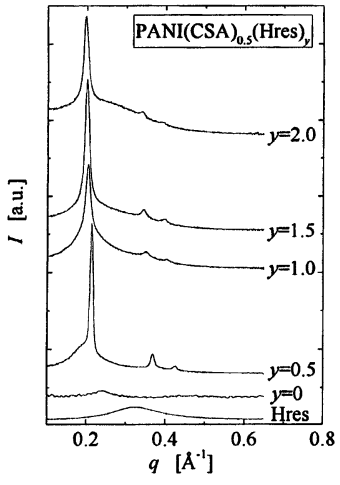

Fig. 2. SAXS patterns of $PANI(CSA)_{0.5}(Hres)_y$ supermolecules indicate that they form cylindrical self-organized structures. The shown data is taken at 105 °C, i.e. above the crystallization temperature of Hres. Qualitatively similar result is obtained at room temperature.

3. Conclusions

Electrically conducting polyaniline supermolecules have been constructed based on hydrogen bonding amphiphiles to allow self-organized cylinders ("nanowires"). Such self-organization increases the conductivity.

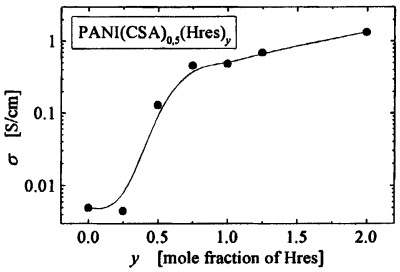

Fig. 3. DC-conductivity of $PANI(CSA)_{0.5}(Hres)_y$ supermolecules as a function of a mole fraction of Hres. Disordered structure is obtained for y=0 and 0.25 whereas cylindrical self-organization for y=0.5, 1.0, 1.5 and 2.0.

Acknowledgements

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